

Article

Polar Vector Property of the Stationary State of Condensed Molecular Matter

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Abstract: Crystalline phases undergoing 180° orientational disorder of dipolar entities in the seed or at growing (hkl) faces will show a polar vector property described by ∞/mm symmetry. Seeds and crystals develop a bi-polar state (∞/mm), where domains related by a mirror plane m allow for a ∞m symmetry in each domain. The polarity of domains is due to energetic favorable interactions at the object-to-nutrient interface. Such interactions are well reproduced by an Ising Hamiltonian. Two-dimensional Monte Carlo simulations performed for real molecules with full long-range interactions allow us to calculate the spatial distribution of the electrical polarization P_{el} . The investigation has been extended to liquid droplets made of dipolar entities by molecular dynamics simulations. We demonstrate the development of an $m\overline{\infty}$ quasi bi-polar state leading to a charged surface.

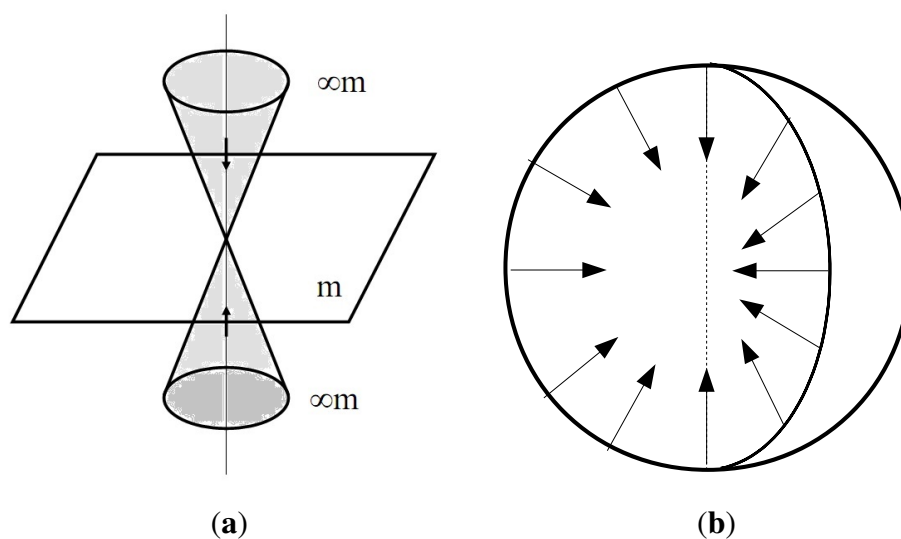
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1. Introduction

Recent experimental and theoretical work [1] lead us to pose a fundamental question: Can mono-domain polar molecular crystals exist [2,3]? Looking at data of the CSD, there seems to be no doubt of a positive answer: roughly 17% of the known structures of molecular compounds [4] (no polymers and proteins) were refined to a polar space group. If we exclude ionic systems (salts) to only consider neutral small molecules, there remain about 9% of the polar structures. Although twinning

and disorder are currently addressed, we notice that only a small number of structural investigations have provided some knowledge on: (i) the absolute orientation of the polar axis in relation to the morphology [5–12]; and (ii) just in a few cases, the spatial distribution of the electrical polarization P_{el} has been analyzed [13–15]. As a matter of fact, we do not know much about the polar domain states of (non-ferroelectric) molecular crystals. By analyzing both the 180° orientational disorder of dipolar entities and the forms of twinning related to the spatial distribution of the polarization, we can, however, answer the aforementioned key question: for crystals expressing a polar morphology by their (hkl) faces, a mono-domain, *i.e.*, a homogeneous polarization distribution, may be observed experimentally [5–12]. This is a kinetic effect due to the critical slowing down occurring in real growth that hinders the reversal transition into a bi-polar state, as predicted by statistical mechanics calculations [2,3] (Figure 1a). This very form of twinning process can, in fact, transform an initial mono-domain polar seed into a final object featuring macroscopic domains of opposite polarities. In this article, we focus on understanding the bi-polar state of condensed matter constituted by polar molecules by symmetry and statistical mechanics arguments. Because of the close analogy, the analysis will also include liquid droplets (Figure 1b) and crystals made thereof.

Figure 1. (a) Bi-polar state ∞/m showing domains (∞m). The polarization may be oriented “down”(as shown) or “up”; (b) Quasi bi-polar state of a stationary spherical object ($m\infty, K_h$).



2. Symmetry and Conservation

The laws of physics are found invariant under the consecutive action of C (charge conjugation), P (parity operation, space inversion, reflection) and T (time reversal) symmetry operations [16]. Molecules and their condensed states are described by quantum and statistical mechanics. The Hamiltonian H_{mol} of a molecular system commutes with each of these operations. Similarly, this holds for molecular crystals made stable by inter-molecular potentials. In our context, parity P is of particular relevance: both the polar vector operators μ_{el} (dipole moment of molecules) and P_{el} (polarization of molecular crystals) change their direction (sign) under the action of P (so, C , not T) [17]. When attempting to calculate

observable properties, such as μ_{el} or P_{el} , we encounter the issue of integrating a state equation over time and space, because for every experiment, a certain time-space domain is committed. In quantum mechanics, the dipole moment μ_{el} is defined by $\int \Psi^* e \mathbf{r} \Psi dV$ (e : charge of the electron; \mathbf{r} : distance vector). Because of:

$$\int \Psi^* e \mathbf{r} \Psi dV = e \int \Psi^* \mathbf{r} \Psi dV = e \int \mathbf{r} |\Psi|^2 dV \quad (1)$$

where the last integrand is the product of a function, \mathbf{r} , with parity odd (−) and $\Psi^* \Psi = |\Psi|^2$ with parity even (+), and since the integral is calculated over the whole space, the expectation value is zero. This is a short hand proof of a statement we can find in textbooks on quantum mechanics [18]: “Quantum-mechanical systems in the stationary state do not have permanent electric dipole moments”. For most molecules, Born–Oppenheimer-based calculations provide a description that can attribute a rigid nuclear frame. This may be extended to a vibronic state; however, the amplitudes of nuclear motion will only cover a small part of the full space of coordinates. Consequently, such a time averaged single object of fixed nuclear conformation (transforming under a polar point group) shows a non-zero dipole moment μ_{el} . Assuming quasi-rigid objects carrying a dipole moment, thermal energy, *i.e.*, temperature, is the variable that will lead to averaging. Consequently, a vector property showing $P = -1$ for single objects will not be observed for a stationary state of an ensemble. However, droplets adopt a bi-polar type of state (Figure 1b), when projecting single dipole moments onto diameters for a summation to yield $\langle P_{\text{el}} \rangle_{\text{zone}}$. Preliminary molecular dynamics (MD) calculations for carbon monoxide in the 2D liquid state show that the oxygen atom of CO molecules is preferentially pointing out of the boundary, whereas towards the center, averaging of $\langle P_{\text{el}} \rangle$ takes place.

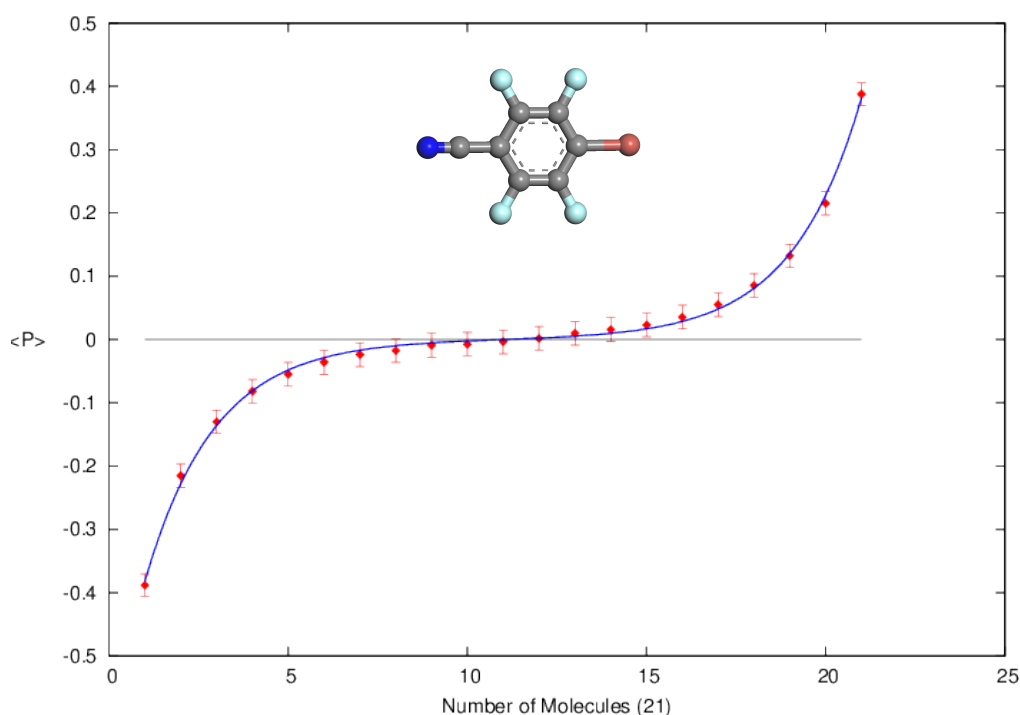
When a liquid-to-solid transition occurs, packing may affect a unique polar axis. Along this axis, physical measurements will find polar vector and higher order uneven rank tensor properties, irrespective of what is giving rise to the polarity: isolated molecules or molecular field-modified entities [19]. Here, we just address the symmetry of the projection of $\langle \mu_{\text{el}} \rangle$ onto this unique axis. The axis itself represents $\infty/m(C_{\infty h})$ symmetry [20]. Because of the finite size of crystals, the mirror plane m gets localized in the middle of the object. This means that the crystal splits into two domains with m perpendicular to the unique axis. A mono-domain polar state is thus not allowed: a polar packing, *i.e.*, the average polarization, is expected to develop a bi-polar state, described by $\infty/mm(D_{\infty h})$ symmetry [20] (Figure 1a). In each domain, a polar vector type property of ∞m symmetry is allowed. For a detailed discussion of the eigensymmetry and the composite symmetry of twinned crystals, see [21] and Figure 3.3.10.2. therein. Considering real crystal structures, *e.g.*, nucleation processes leading to n/m ($n = 2, 3, 4, 6$) point groups and growth along the axis n , the stochastic process transforms pro-chiral faces into chiral sectors. Because of the mirror plane m passing through a seed, sectors involving the $+n$ or the $-n$ direction show an enantiomorphic relation (for a discussion of other point groups and low index faces, see [22]).

So far, the bi-polar state for molecular crystals was experimentally demonstrated by scanning pyroelectric and phase-sensitive second harmonic microscopy [1]. Here, the measurement of the circular dichroism of each sector could add a third proof for a stochastic mechanism of symmetry lowering.

What may be a mechanism by which a molecular packing can attain a bi-polar state? By the 180° orientational disorder of dipolar building blocks: Monte Carlo (MC) simulations [2,3] have suggested

a growth-induced stochastic reversal transition for building blocks, when starting from a polar seed, ending up in a bi-polar state. At this point, we turn to the seed itself. What will be the polar state of dipolar molecules aggregating in a nucleus leading to further crystallization? MC simulations based on a simple interaction scheme [2,3] have shown that a 3D system adopts a bi-polar state. Most recently, MC simulations with full long range interactions confirmed [23] this behavior for a 2D array of acceptor-donor-substituted benzene molecules (Figure 2).

Figure 2. Average polarization vs. lattice site for an MC 2D-simulation, showing the bi-polar state formation. The full line is the fit with an exponential function. The system is composed of 21×5 molecules (1-bromo-4'-cyano-tetrafluoro-benzene) arranged in five parallel chains.



For both MC-type simulations, many random initial orientational states for the entities are employed for the average of the quantities of interest. From there, the system evolves into a bi-polar state. Analogously, when starting from an ordered, but centric seed, MC growth also results in a bi-polar state [2,3], producing a certain degree of polar alignment in each of the domains. As presented so far, the bi-polar state was demonstrated by simulations. An Ising [24] model describing a system of interacting adjacent chains allows us to understand that opposite average polarities can exist in each of the domains. The spin Hamiltonian H (Equation (2)) has been derived in two dimensions, under very general assumptions: (i) for any given state configuration $S_i = \pm 1, i = 0, \dots, N$, Equation (2) is the energy of that configuration; (ii) periodic boundary conditions on the transverse direction and a free boundary condition on the longitudinal one.

$$H = \epsilon + \Delta E_f \sum_j (S_j(0) - S_j(N)) + \sum_{ij} [S_{j+1}(i)S_j(i)\Delta E_{\perp}/2 - S_{i+1}(j)S_i(j)(\Delta E_A + \Delta E_D)/4] \quad (2)$$

where $\Delta E_{\perp} = E_{\text{par}} - E_{\text{antip}}$, where E_{par} (resp. E_{antip}) is the energy of two next-neighbor spins parallel (resp. anti-parallel), due to the transverse interaction. The sums are taken over all lattice

points, specifically, i and j run over the longitudinal and transverse direction, respectively; ϵ is a constant term. Whereas the bilinear terms (longitudinal and transverse interactions) can induce polar alignment of vectors, they do not provide a definite direction of polarity $\langle P_{el} \rangle$. Absolute polarity (directionality) is introduced by the linear effective particle operators S_0 and S_N in H . These terms are formally equivalent to the action of an electrical field E , representing and, thus, introducing ∞m [20,25], *i.e.*, polar vector symmetry. The energy parameter ΔE_f [2,3] associated with these two linear terms in H reflect the polar symmetry of interacting molecules: in a simple description of the interactions, ΔE_f is equal to $E_{AA} - E_{DD}$, *i.e.*, the difference in the energy for defect formation in a single chain: $E_{AA} : -A \cdots A -$; $E_{DD} : -D \cdots D -$ (A: acceptor; D: donor). Therefore, at each border of the unique axis, an effective field (∞m) [25] is reducing the symmetry of the axis to yield a polar vector property (∞m ; also chiral ∞) in each domain. It can be shown that the introduction of the ΔE_f energy parameter is not restricted to nearest neighbor interactions, but can be extended to a lattice sum.

3. Summary and Conclusions

One main point emerges from this study: in the case of a crystal lattice, (i) the early (nucleation) or (ii) the later state (growth) can accommodate 180° *orientational defects of dipolar entities* (Figure 1b); both the seed and the final crystal will show a polar vector property described by ∞/m ($D_{\infty h}$) [20] symmetry, *i.e.*, a bi-polar state (Figure 1a), where domains related by a mirror plane m show a polar vector property (∞m , $\langle P_{el} \rangle$) induced by the linear terms $\Delta E_f S_i (i = 0, N)$ in H (Equation (2)). This general behavior predicted by H was reproduced by different types of MC and MD simulations, assuming either a simple nearest neighbor interaction scheme [2,3] or long-range interactions of real molecules (Figure 2).

Did we properly answer our initial question? There is one important point left out so far: in case molecules by kinetic control, *i.e.*, nucleation at high supersaturation/supercooling, form a mono-domain polar seed (instead of a well-thermalized bi-polar object), this state may persist up to a macroscopic size, because the probability to undergo the reversal transition [2,3] may be too small to occur up to the final size that a crystal can attain. It is, therefore, likely to find crystals representing a polar morphology and a mono-domain state. Nevertheless, our final conclusion is the mono-domain polar molecular crystals, for reasons of symmetry and orientational defects (configurational entropy), should not exist.

Acknowledgments

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Author Contributions

Jürg Hulliger: general theoretical frame; Luigi Cannavacciuolo: MC simulations, Hamiltonian; Mathias Rech: Hamiltonian and basic physics.

Conflicts of Interest

The authors declare no conflict of interest.

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